

Supporting Information

Green synthesis of carbon quantum dots from lemon peel waste: Applications in sensing and photocatalysis

Ankit Tyagi,^{al} Kumud Malika Tripathi,^{al} Narendra Singh,^{a,b} Shashank Choudhary,^a
and Raju Kumar Gupta^{*a,b}

^a Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur-208016, UP, India

^b Center for Nanosciences and Center for Environmental Science and Engineering, Indian Institute of Technology Kanpur, Kanpur-208016, UP, India

*Corresponding author. Tel: +91-5122596972; Fax: +91-5122590104.

E-mail address: guptark@iitk.ac.in

^l Contributed equally.

Characterization techniques

Fourier transform infrared (FTIR) spectra of the wsCQDs were analyzed with Bruker Fourier transform infrared spectrometer (Vector 22 model) using KBr pellets. Zeta potential measurement was done in aqueous solution with Malvern Zetasizer Nano ZS 90 to measure the surface charge on wsCQDs. Thermogravimetric analysis (TGA) was carried out by using a C. I. electronics analyzer on a SDTQ600, TA instruments, (waters LLC, 159 Lukens Drive, New Castle DE 19720) in nitrogen atmosphere at heating rate of 10 °C-min⁻¹ and amount of wsCQDs loading over TiO₂ nanofibers was found using TGA. The surface morphology of the wsCQDs and TiO₂-wsCQDs composites was done by using field-emission scanning electron microscopy (FESEM) SUPRA 40VP, Carl Zeiss (NTS GmbH, Oberkochen, Germany) microscope operated at 10 kV in high vacuum mode and by using transmission electron microscopy (TEM) (Tecnai 20 G2 STWIN model) at an accelerating voltage of 200 kV. Samples for TEM characterization were prepared by drop casting 5 µL aqueous solution onto a carbon coated copper grid (mesh size 400) and vacuum dried. UV-visible absorption spectra were performed by Double beam UV-visible spectrometer (Varian Cary 100,

Germany). Perkin Elmer LS 55 spectrophotometer was employed to record photoluminescence (PL) behavior. The PL spectra were recorded at room temperature in aqueous solutions. X-ray photoelectron spectroscopic (XPS) measurements were carried out with PHI 5000 Versa Probe II, FEI Inc. spectrometer. The XPS binding energy values for wsCQDs were charge-corrected placing the main C 1s peak at 284.6 eV. XRD pattern of TiO₂ nanofibers and TiO₂-wsCQDs composite were recorded using PANalytical, Netherlands with X-ray source of wavelength (1.5406 Å).

Quantum yield determination of wsCQDs

The relative quantum yield of synthesized wsCQDs was measured with reference to quinine sulphate as reported earlier¹ by using following equation:

$$Q_x = Q_{ST}(I_x/I_{ST})(A_{ST}/A_x)$$

where Q is the quantum yield of wsCQDs, I is the measured intensity of fluorescence emissions, and A is the absorbance. ST represents to the standard and x represents the sample. The comparative emission intensity of wsCQDs after one year of storage (red line) and fresh solution (black line) at 360 nm excitation wavelength is shown in Figure S1.

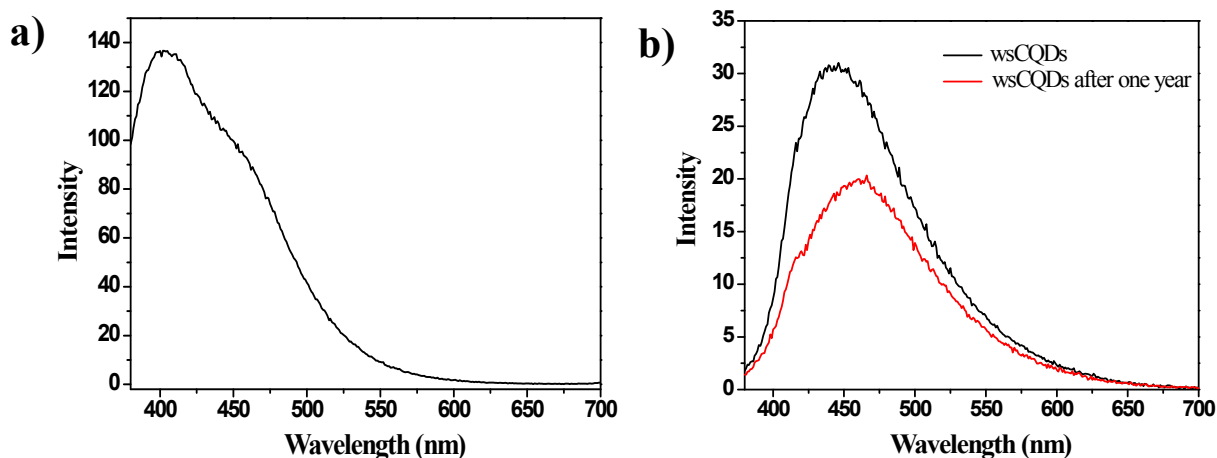


Fig. S1 (a) PL emission spectra of reference quinine sulfate; (b) Comparative PL emission of wsCQDs fresh (black line) and after one year of storage (red line) at 360 nm excitation wavelength.

Table S1. Comparison of quantum yield of CQDs derived from lemon peel waste with the reported CQDs

Carbon Source	Synthesis method	Application	QY(%)	Reference
Pomelo peel	Hydrothermal	Hg ²⁺ sensing	6.9	2
Aloe	Hydrothermal	Tartrazine sensing	10.4	3
Soy milk	Hydrothermal	Electrocatalyst for oxygen reduction	2.6	4
Honey	Hydrothermal	Fe ³⁺ detection	19.8	5
Graphite rod	Electrochemical exfoliation	Photocatalytic activity	16.5	6
Eggshell membrane	Microwave assisted	Glutathione sensing	14	7
Willow bark	Hydrothermal	Glucose detection	6	8
Flour	Microwave assisted	Hg ²⁺ detection	5.4	9
Graphite powder	Laser ablation	-----	4.0-10	10
Carbon soot	Arc discharge	-----	1.6	11
Chicken eggs	Plasma induced	Fluorescent carbon inks for printing	6-8	12
Lemon peel	Hydrothermal	Cr ⁶⁺ sensing and photocatalytic activity	~14	This work

Table S2. Performance comparison among various fluorescence based sensors toward Cr⁶⁺ detection

Fluorescent sensor	Response time	Detection limit	Reference
Rhodamine B hydrazide	60 min	$5.5 \times 10^{-9} \text{ mol L}^{-1}$	13
CdTe quantum dots	40 min	$0.008 \text{ } \mu\text{g mL}^{-1}$	14
N-Doped graphene quantum dots	NA	40 nM	15
Hydrophilic ionic chemosensor	30 s	$9.2 \times 10^{-8} \text{ M}$	16
Glutathione-stabilized gold nanoclusters	30 min	$2.5 \text{ } \mu\text{g L}^{-1}$	17
N, S-Doped carbon dots	NA	20 nM	18
Perylene nanoparticles	NA	$0.008 \text{ } \mu\text{g mL}^{-1}$	19
wsCQDs	1 min	73 nM	This work

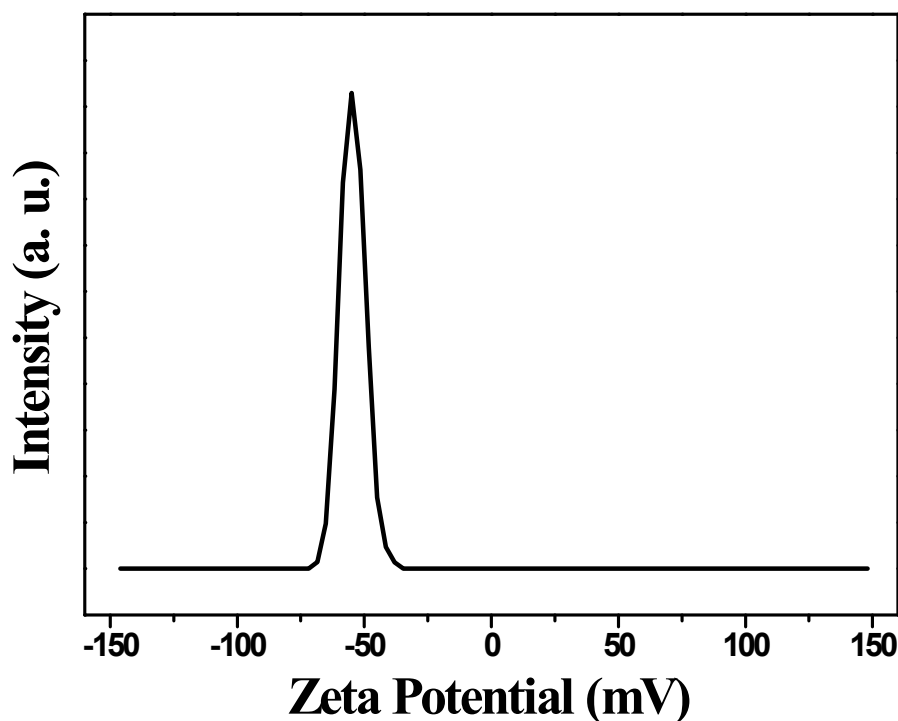


Fig. S2 Zeta potential curve for aqueous solution of wsCQDs at 25 °C.

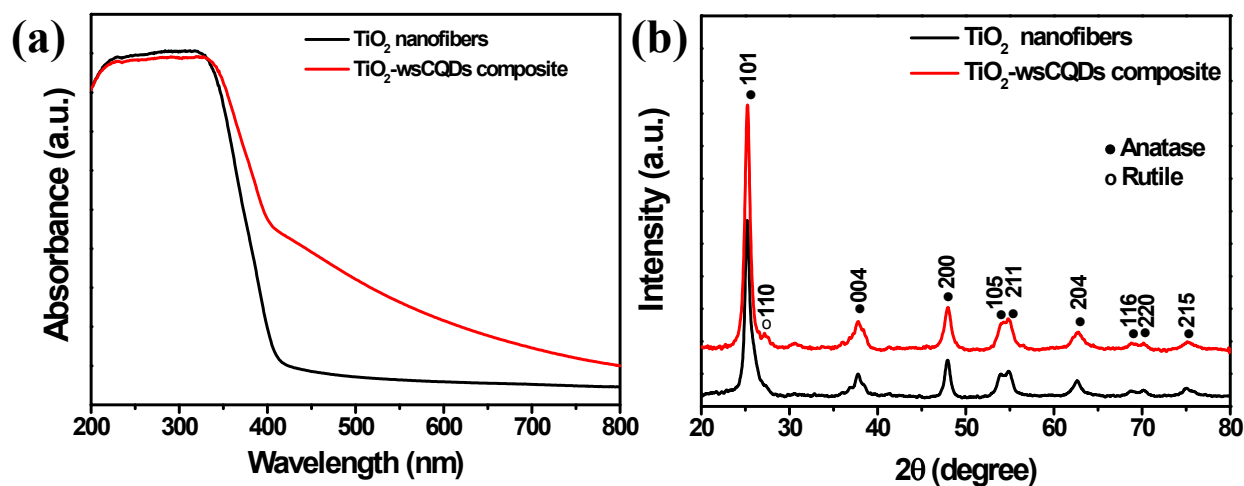


Fig. S3 (a) UV-vis spectra TiO₂ nanofibers and TiO₂-wsCQDs composite; (b) XRD spectra of TiO₂ nanofibers and TiO₂-wsCQDs composite.

Photocatalytic reaction steps:

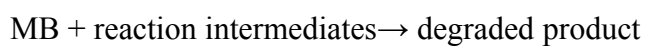
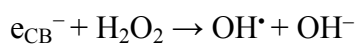
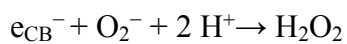
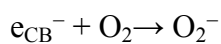
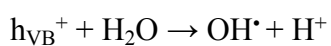
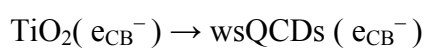
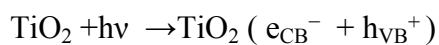


Table S3. Photocatalytic performance comparison with other carbon dot heterostructures

Material	Morphology	Pollutant	% Increase in photocatalytic activity	Reference
TiO ₂	Particle	RhB	24	20
ZnO foam	Nanoparticle	RhB	~8	21
TiO ₂	Nanobelt	MO	~23	22
ZnO	Chain like	Naphthol blue-black	15.7	23
Graphitic carbon nitride	Chiffon-like ripples and wrinkles	RhB	~56	24
ZnO	Particle	RhB	50	25
TiO ₂	Nanofiber	MB	31	This work

References

1. K. M. Tripathi, A. K. Sonker, A. Bhati, J. Bhuyan, A. Singh, A. Singh, S. Sarkar and S. K. Sonkar, *New J. Chem.*, 2016, **40**, 1571-1579.
2. H. Yu, Y. Zhao, C. Zhou, L. Shang, Y. Peng, Y. Cao, L.-Z. Wu, C.-H. Tung and T. Zhang, *J. Mater. Chem. A*, 2014, **2**, 3344-3351.
3. F. Li, F. Tian, C. Liu, Z. Wang, Z. Du, R. Li and L. Zhang, *RSC Adv.*, 2015, **5**, 8389-8396.
4. M. R. Hoffmann, S. T. Martin, W. Choi and D. W. Bahnemann, *Chem. Rev.*, 1995, **95**, 69-96.
5. M. Montazer and E. Pakdel, *J. Photochem. Photobiol. C: Photochem. Rev.*, 2011, **12**, 293-303.
6. M. N. Chong, B. Jin, C. W. K. Chow and C. Saint, *Water Res.*, 2010, **44**, 2997-3027.
7. Q. Wang, X. Liu, L. Zhang and Y. Lv, *Analyst*, 2012, **137**, 5392-5397.
8. X. Qin, W. Lu, A. M. Asiri, A. O. Al-Youbi and X. Sun, *Catal Sci Technol*, 2013, **3**, 1027-1035.
9. N. Dhenadhyalan, K.-C. Lin, R. Suresh and P. Ramamurthy, *J. Phys. Chem. C*, 2016, **120**, 1252-1261.
10. Y.-P. Sun, B. Zhou, Y. Lin, W. Wang, K. A. S. Fernando, P. Pathak, M. J. Mezziani, B. A. Harruff, X. Wang, H. Wang, P. G. Luo, H. Yang, M. E. Kose, B. Chen, L. M. Veca and S.-Y. Xie, *J. Am. Chem. Soc.*, 2006, **128**, 7756-7757.
11. X. Xu, R. Ray, Y. Gu, H. J. Ploehn, L. Gearheart, K. Raker and W. A. Scrivens, *J. Am. Chem. Soc.*, 2004, **126**, 12736-12737.
12. J. Wang, C.-F. Wang and S. Chen, *Angewandte Chemie International Edition*, 2012, **51**, 9297-9301.
13. Y. Xiang, L. Mei, N. Li and A. Tong, *Analytica Chimica Acta*, 2007, **581**, 132-136.
14. L. Zhang, C. Xu and B. Li, *Microchimica Acta*, 2009, **166**, 61-68.
15. F. Cai, X. Liu, S. Liu, H. Liu and Y. Huang, *RSC Adv.*, 2014, **4**, 52016-52022.
16. D. Zhang, Z. Dong, X. Jiang, M. Feng, W. Li and G. Gao, *Analytical Methods*, 2013, **5**, 1669-1675.
17. H. Zhang, Q. Liu, T. Wang, Z. Yun, G. Li, J. Liu and G. Jiang, *Analytica Chimica Acta*, 2013, **770**, 140-146.
18. Y. Liu, X. Gong, Y. Gao, S. Song, X. Wu, S. Shuang and C. Dong, *RSC Adv.*, 2016, **6**, 28477-28483.

19. D. K. Dalavi, D. P. Bhopate, A. S. Bagawan, A. H. Gore, N. K. Desai, A. A. Kamble, P. G. Mahajan, G. B. Kolekar and S. R. Patil, *Analytical Methods*, 2014, **6**, 6948-6955.
20. W. Wang, Y. Ni and Z. Xu, *J. Alloys Compd.*, 2015, **622**, 303-308.
21. D. Ding, W. Lan, Z. Yang, X. Zhao, Y. Chen, J. Wang, X. Zhang, Y. Zhang, Q. Su and E. Xie, *Materials Science in Semiconductor Processing*, 2016, **47**, 25-31.
22. J. Tian, Y. Leng, Z. Zhao, Y. Xia, Y. Sang, P. Hao, J. Zhan, M. Li and H. Liu, *Nano Energy*, 2015, **11**, 419-427.
23. A. Prasannan and T. Imae, *Ind. Eng. Chem. Res.*, 2013, **52**, 15673-15678.
24. S. Fang, Y. Xia, K. Lv, Q. Li, J. Sun and M. Li, *Applied Catalysis B: Environmental*, 2016, **185**, 225-232.
25. Y. Li, B.-P. Zhang, J.-X. Zhao, Z.-H. Ge, X.-K. Zhao and L. Zou, *Appl. Surf. Sci.*, 2013, **279**, 367-373.